



Kinetic study and H₂S effect on refractory DBTs desulfurization in a heavy gasoil

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ABSTRACT

The removal evolution of six refractory individual S-compounds, i.e. DBT, 4-methyl-DBT, 4,6-dimethyl-DBT, 4-ethyl-6-methyl-DBT, 2,4,6-trimethyl-DBT, and 2,4,6,8-tetramethyl-DBT, and five groups of S-compounds with one to four substitutions has been studied during the deep desulfurization process of a heavy gasoil in a mini scale-structured bed reactor. The reactivity of the sulfur compounds was investigated by hydrotreating the gasoil with a commercial NiMo/γ-Al₂O₃ catalyst under commercial operation conditions of temperature (563–623 K), total pressure (50 × 10⁵ Pa), liquid hourly space velocity (LHSV) (0.7–3 h⁻¹), and gas-to-liquid ratio (400–600 Nm³_{H₂}/m³_{oil}). Moreover, the inhibiting effect of the hydrogen sulfide on the hydrodesulfurization rates of the S-compounds has been studied by performing tests with various H₂S partial pressures. The results showed that the most refractory sulfur component is the 4,6-dimethyl-DBT constituting the major compound in the hydrotreated product with 50 ppm total sulfur and practically the only S-compound in the product with 10 ppm total sulfur. It has been verified that differences in HDS reactivity among DBT, 4-methyl-DBT, and 4,6-dimethyl-DBT in the real feed are lower than those commonly referred to in model feeds. The reactivity of the S-compounds is affected by the presence of the adsorbed on the catalyst active sites hydrogen sulfide and this effect appears decreasing with the number of the substituents of DBTs. The activation energy of DBTs obtained in the current work appears to be higher for the non-substituted DBT, which mainly reacts through the hydrogenolysis route, and to decrease for the substituted DBTs, which react through the hydrogenation route.

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1. Introduction

Environmental and human life's quality requirements have led countries to set very strict specifications for the sulfur content in the transportation fuels, aiming at SO₂ reduction in car exhaust gases for its disposal elimination and protection of catalytic converters [1]. The commission of the European Community has instituted that all petrol and diesel sold in its area must contain less than 10 ppm after January 1st of 2009 [2–4]. Thus, the deep desulfurization of the oil fractions is in the forefront of the investigation topics in the modern refineries. To this end the main targets are the development of new and/or the improvement of existing processes for the catalytic hydrotreatment of the petroleum fractions by inventing new and more efficient catalysts, by optimizing the operating conditions of the existing units [5–8], and by increasing the effectiveness and the operation life of the existing catalysts monitoring their activity online [9].

For the study of the conventional HDS processes the researchers have focused their interest on the investigation of the reaction mechanisms of Dibenzothiophene (DBT) and its alkyl-derivatives. These compounds and especially the DBTs with substituents at 4

and 6 positions appear to be very refractory in the HDS process of several oil fractions with sulfur content in the products less than 1000 ppm [10–15]. Some researchers have published the studies on the sulfur removal mechanism of DBT, 4-methyl-DBT, 4,6-dimethyl-DBT, and other DBTs in synthetic feeds containing one model S-compound or in mixtures with two or three individual model S-compounds [10–13,16–23]. Some others have investigated the evolution of the concentration of individual S-compounds in real feeds helped by new analytical methods for the determination of the individual S-compounds content in oils [24–34]. A generally accepted observation concerns the strong inhibiting matrix effect of the gasoil molecules on the HDS reaction rates of the sulfur compounds [26] and the small differences between the HDS reaction rate constants of DBTs present in the light gasoil as compared with those measured for the pertinent model S-compounds in the artificial mixtures [31]. The matrix effect originates from various molecules of the oil which are present and competitively to the reacting molecules adsorbed on the catalyst surface.

The results of both sorts of studies regarding the mechanisms of DBTs removal, i.e. with synthetic and real feeds, agree that the DBTs are transformed through two parallel routes, the direct desulfurization route (DDS) by cleavage of the C–S bonds giving biphenyl and hydrogen sulfide and the indirect route (HYD) with a primary hydrogenation reaction giving hydrodibenzothiophenic

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intermediates, and finally producing cyclohexylbenzenes and bicyclohexyls [16]. The DBT and the DBTs with substituents at different to 4 and 6 positions, like 2,8-dimethyl-DBT and 3,7-dimethyl-DBT are mainly transformed via the direct route while the others, like 4-methyl-DBT and 4,6-dimethyl-DBT are mainly transformed through the indirect route [10,11,14–16,19,20,23,35,36].

As to the common catalysts used for the HDS procedure, it is considered that the NiMo/Al₂O₃ catalysts are superior to CoMo/Al₂O₃ ones as hydrogenation catalysts and inferior as HDS catalysts. Thus NiMo/Al₂O₃ catalysts appear more appropriate for the conversion of 4,6-dimethyl-DBT [15,36] while CoMo/Al₂O₃ catalysts are preferable for DBT and other DBTs without substituents at 4 and 6 positions. Gates and Topsoe [15] presented results from HDS experiments of individual S-compounds at 623 K and 50 bar and they noticed that the ratio of the HDS reaction rate constants of 4,6-dimethyl-DBT on NiMo-P/Al₂O₃ and CoMo/Al₂O₃ catalyst is 1.61 while for 4-methyl-DBT it is referred to be 1.01 and for DBT it is 0.76.

For the explanation of the differences in the reactivity rates, there are different hypotheses in the literature concerning the two different routes involved in the HDS of DBTs. Houalla et al. [14] proposed that the low reactivity of DBTs with substituents at positions 4 and 6 was due to steric effects on adsorption. They claimed that the adsorption strength decreases in the order DBT > 2,8-dimethyl-DBT > 3,7-dimethyl-DBT > 4-methyl-DBT > 4,6-dimethyl-DBT and they proposed that there are two different kinds of adsorption of the S-components on the catalyst; a vertical adsorption through the compound S-atom, related with the direct route of HDS, and a flat adsorption through the π -electrons of the aromatic system related with the indirect route of HDS. Similar proposal has been made by Li et al. [23], Ramirez et al. [33], Kim et al. [36], Egorova and Prins [37].

In contrast, Singhal et al. [38] suggested that all DBTs adsorb on the catalyst through the π -electron in their aromatic rings and the HDS mechanism involves first a preliminary partial hydrogenation of the adsorbed aromatic system and then the desulfurization route or the hydrogenation route occurs. This hypothesis is also supported by Mielle et al. [11] and Bataille et al. [12].

Although Kabe et al. [39] did not refer to the first, preliminary partial hydrogenation step, they agree that the DBTs with substituents at 4 and 6 positions adsorb on the catalyst active sites through the π -electron in their aromatic rings and they suggested that the adsorption of DBTs are not hindered by the methyl substituents but the C–S bond scission is prevented by the methyl substituents. In the same way Mielle et al. [11], Bataille et al. [12], and Milenkovic et al. [21] supported that all the S-compounds they studied (Milenkovic: 4,6-dimethyl-DBT, 4,6-diethyl-DBT; Mielle: 4,6-diisobutyl-DBT for the first and DBT, 4-MDBT, 4,6-DMDBT, and 2,8-DMDBT) were identically adsorbed on the catalytic surface and probably via the π -electrons and thus adsorption strength was not responsible for the difference of their reactivity. They claimed that the differences in their transformation reactivity is related to the lower reaction rates of the C–S bond cleavage (elimination reaction) due to steric hindrance in the basic attack by the alkyl group near the sulfur atom.

Egorova and Prins [37], Broderick et al. [40], Edvinson and Irandoust [41], and Froment [42] claimed that hydrogenolysis takes place on one kind of sites, type σ , while hydrogenation step may occur on different sites which are called τ , following the indirect route. In the latter case, the hydrogenated hydrodibenzothiophenic intermediates undergo HDS on σ sites. Froment [42] mentioned also that on σ sites DBTs without substituents are adsorbed vertically through its S-atom as well as the product H₂S. On the τ -sites flat adsorption is considered. Egorova and Prins [37] proposed that the desulfurization via the DDS and HYD pathways occurs over the same active sites and that a similar mecha-

nism of sulfur removal is involved in the DDS pathway and in the final step of the HYD pathway. Also, they explained that the methyl groups suppress the adsorption not only of the reactant on the σ -active sites but also of the partially hydrogenated intermediates on them. Meille et al. [11] claimed that the HDS of all DBTs occurs on one type of sites in a flat adsorption mode.

The S-compound reactivity is inhibited by several components and by-products during HDS process. Schulz et al. [26] and Yang et al. [30] mention that the inhibition effect decreases in the order: basic nitrogen compounds > organic sulfur compounds > H₂S > condensed aromatics \approx oxygen compounds > saturated and mono-aromatic hydrocarbons. It is generally accepted that the active sites responsible for hydrogenation are more susceptible to nitrogen poisoning than those responsible for hydrogenolysis [30,43,44].

Most of the works have also focused on the investigation of hydrogen sulfide inhibition effect on the DBTs' desulfurization rates [10–12,18–20,22,26,32,45] because real feeds hydrotreatment is performed in the presence of high H₂S partial pressures.

It is generally admitted that NiMo/Al₂O₃ catalysts are affected to a greater extent than CoMo/Al₂O₃ catalysts by H₂S [32,37,45,46]. However, opposite conclusions have also been reported by Rabarihoela-Rakotovoao et al. [13] and by Kabe et al. [22] who refer that the effect of H₂S on the catalyst activity increases in the order NiMo < NiW < CoMo.

Results have also been presented proving that although H₂S inhibits both the HDS rates of DBT and 4,6-dimethyl-DBT on CoMo and NiMo catalysts, the HDS of DBT is more influenced than that of 4,6-dimethyl-DBT [11–13,19,20,22,37]. The differences in H₂S influence on the HDS reactivities of DBT and 4,6-dimethyl-DBT is attributed to the different contribution of the routes followed by the S-compounds during their transformation. It has been proposed that the DDS (direct desulfurization) pathway, which DBT mainly follows, is more affected by H₂S than the HYD (hydrogenation) pathway which is mainly followed by 4,6-dimethyl-DBT. Moreover, Rabarihoela-Rakotovoao et al. [13] refer that the DDS route is more affected by H₂S for DBT desulfurization than for 4,6-dimethyl-DBT. The same conclusion comes up from the results of other researchers [11,12].

Considering the knowledge offered by the previous works, the study of hydrodesulfurization of DBTs with more than two substituents in artificial feeds with model S-compounds as well as in real feeds would be useful for further extending the discussion about the reaction scheme of DBTs as well as to clarify the role of the substituents in HDS mechanisms. Although several works have studied the HDS of poly-aromatic sulfur compounds, more detailed investigation is required in order to explain and enlighten the conflicting discussions and conclusions [15,24,25,29,30,32].

In this work, the HDS of various DBTs in a real feed is studied using a common NiMo/ γ -Al₂O₃ catalyst and the effect of the number and the position of the substituents on the rates of sulfur removal is discussed. Also, the influence of the hydrogen sulfide on the HDS rates of the DBTs is examined.

2. Experimental section

2.1. Materials

Desulfurization experiments of heavy gasoil with initial sulfur content of 1.3% w/w were carried in a variety of industrial experimental conditions. The properties of the feed are presented in Table 1. The determination of the total sulfur content in the liquid feed as well as in the HDS products was carried out with an Antek 9000 Series sulfur analyzer while the content of the individual S-species was determined by a S-sensitive gas chromatograph

Table 1
Properties of the feed.

Physical properties	$d_{15/4}$ (g/ml)	0.854
	$R_{I_{20^{\circ}C}}$	1.476
	MW	259
Chemical properties	S (% wt)	1.341
	N (ppm)	127.0
	H (% wt)	13.25
Distillation curve (K)	10% (vol)	534
	30% (vol)	560
	50% (vol)	579
	70% (vol)	598
	90% (vol)	623

(Varian CP-3800, pulsed flame photometric detector, PFPD) [4,5]. Peak identification was based on reference S-species and literature data.

The sulfur contained in the various DBT molecules of the feed was classified into five groups and six specific compounds. The five S-groups consisted of the following S-components: the methyl-DBT group included the DBT compounds with one methyl substitute at different to 4 positions (Fig. 1, [15]), the dimethyl-DBT group included the DBT compounds with two methyl substituents except of 4,6-dimethyl-DBT, the trimethyl-DBT group included the DBT compounds with three methyl substituents except of 2,4,6-trimethyl-DBT, the tetramethyl-DBT group included the DBT compounds with four methyl substituents except of 2,4,6,8-tetramethyl-DBT, and the pentamethyl-DBT group included DBTs with five methyl substituents. The individual S-compounds identified in the gasoil are the DBT, the 4-methyl-DBT, the 4,6-dimethyl-DBT, the 4-ethyl-6-methyl-DBT, the 2,4,6-trimethyl-DBT, and the 2,4,6,8-tetramethyl-DBT.

2.2. Apparatus and procedure

The desulfurization experiments were carried out in a mini-scale laboratory unit the flow sheet of which is shown in Fig. 2. The unit operates unattended in a fully automated mode. The main parts of the unit are the reactor bed, a high pressure gas–liquid separator, a piston pump to feed the reactor with liquid, and a hydrogen cylinder. Proper systems have been developed to control the operation of the unit and to switch it off in case of emergency or maloperation. Finally, a proper system has been constructed for the replacement of the sodium hydroxide solution used to absorb the hydrogen sulfide from the gas effluent stream during the operation of the unit [9,47].

For the experiments presented in this work, a three-phase spiral reactor was used. Some of the main features of the spiral reactor operation have been presented in a previous work [47]. The spiral reactor imposes the gas and the liquid phase to flow over all particles, avoiding bypassing and flow maldistributions. It has been shown that the repeatability as well as the stability of the spiral reactor operation is satisfactory even for very low gas and liquid velocities. Also, the operation of the spiral reactor was proven quite successful even at ultra deep hydrodesulfurization conditions (<5–

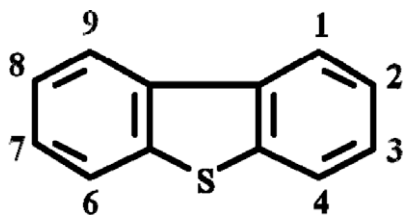


Fig. 1. DBT molecule and positions of methyl substituents.

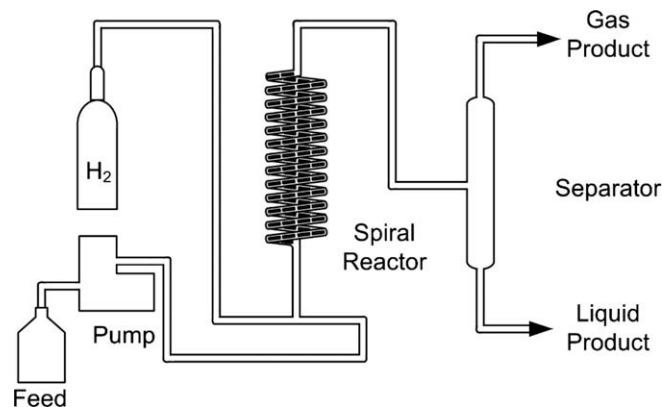


Fig. 2. Flow sheet of the laboratory mini-scale HDS unit.

10 ppm_S in the product). Finally, performing experiments in a wide range of gas and liquid velocities, temperatures, and gas-to-liquid ratios, it appeared that the spiral reactor operation is not affected by its length and catalyst loading. This implies that downscaling effects such as wall channeling, axial backmixing, liquid-to-solid mass transfer resistances and incomplete catalyst particle irrigation do not affect its operation.

A 6 m long spiral reactor was built in a 2.1 mm internal diameter tube with a sample of 8.3×10^{-3} kg trilobate NiMo/ γ -Al₂O₃ catalyst. The mean diameter of the catalyst extrudates was 1.1 mm while the mean catalyst length was 4 mm. From experiments carried out in our Laboratory with crushed catalyst particles and extrudates it has been proven that the effectiveness factor of the extrudates was more than 0.87 for all the experimental conditions of this work. Similar approximation has been followed by many other researches [4,5,24,25,27–29,31–33,48].

Before starting the experiments the catalyst was sulfided for about 35 h. A light gasoil with 2% wt. Dimethyl disulfide (DMDS) was used for sulfidation at hydrogen pressure 50×10^5 Pa, LHSV = 1.5 h^{-1} and gas to oil ratio 200. During sulfidation the temperature was linearly increased from room temperature up to 623 K within 20 h and then it was kept constant at 623 K for a period of 15 h. After the sulfidation and before the beginning of the hydrodesulfurization experiments the catalyst was stabilized by running the unit at LHSV: 1.0 h^{-1} , temperature: 613 K, gas to liquid ratio $400 \text{ Nm}^3/\text{m}^3$ and absolute hydrogen pressure 50×10^5 , for four weeks [30,33]. The initial activity of the catalyst decreased during the first four weeks and it reached a constant level at the end of the fourth week. During HDS experimentation, the activity of the catalyst was checked to be unchanged by performing reference run at the conditions of the stabilization period and time intervals of 40–50 h.

The experiments were performed at LHSV values 0.7, 1.0, 2.0 and 3 h^{-1} , temperature between 563 and 623 K, gas to liquid ratio $400 \text{ Nm}^3/\text{m}^3$ and absolute hydrogen pressure 50×10^5 Pa at co-current upflow mode. Also, in order to study the impact of the hydrogen sulfide on the decomposition rates of the sulfur compounds, desulfurization experiments were performed with the same gasoil at common HDS conditions but varying the partial pressure of hydrogen sulfide by adding the appropriate amount of dimethyl-disulfide in the liquid feed.

3. Results and discussion

3.1. HDS kinetic study of the DBT compounds

The results of the heavy gasoil hydrodesulfurization experiments, taking into account first-order kinetics, are presented for

the group compounds in Fig. 3 and for the specific compounds in Fig. 4. The term $C_{i,OUT}$ (ppm w/w) represents the concentration of each group or individual S-compound in the hydrotreated products while the $C_{i,FEED}$ (ppm w/w) represents the concentration of the same S-compound in the feed. Similar approximations have been presented in a few other works [29–32]. As it is shown, the removal rates of the sulfur compounds can be satisfactorily described by the pseudo-first order kinetic model, in line with the published results for similar and the same compounds.

The apparent HDS rate constants (k_{HDS}^{app}) of the groups and the individual S-compounds evaluated from the slopes of Figs. 3 and 4 are presented in Fig. 5. From these results it is clear that the highest reactivity is obtained for the non-substituted DBT while the group methyl-DBT reactivity is the second highest one. The reactivities of the other groups of S-compounds do not seem to vary significantly. The reactivity estimated for each group represents a mean reactivity of all poly-DBTs except of the ones with substituents at positions 4 and 6. Thus, the reactivity of each compound of the group is higher than that of the respective individual DBT with substituents at positions 4 and 6.

Among the individual S-compounds it is observed that the reactivity of DBT is the highest one. The higher reactivity among the substituted individual S-compound is observed for 4-methyl-DBT that is slightly lower than the reactivity of methyl-DBT group which consists of DBTs with a substitute at a different to 4 positions.

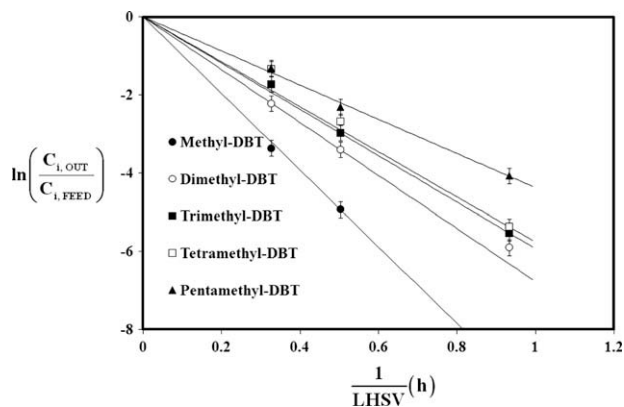


Fig. 3. First-order kinetics plot of methyl-DBT, dimethyl-DBT, trimethyl-DBT, tetramethyl-DBT, and pentamethyl-DBT groups hydrodesulfurization. Temperature: 613 K. Hydrogen Pressure: 50×10^5 Pa. Gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$.

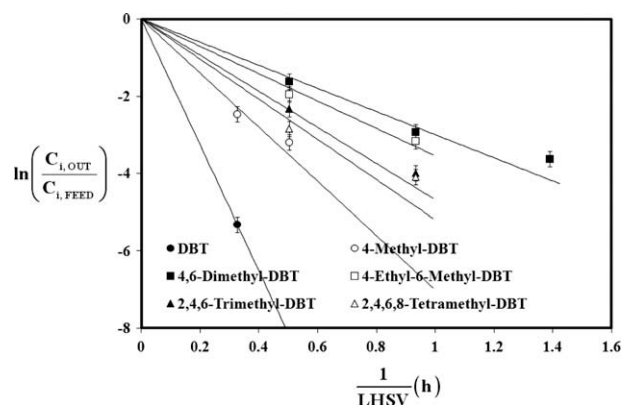


Fig. 4. First-order kinetics plot of DBT, 4-methyl-DBT, 4,6-dimethyl-DBT, 4-ethyl-6-methyl-DBT, 2,4,6-trimethyl-DBT, and 2,4,6,8-tetramethyl-DBT hydrodesulfurization. Temperature: 613 K. Hydrogen pressure: 50×10^5 Pa. Gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$.

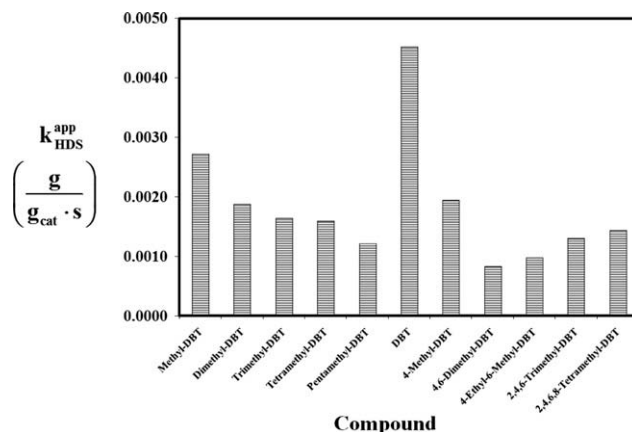


Fig. 5. Apparent reaction rate constants of DBTs groups and DBTs individual compounds. Obtained for LHSV: $1-3 \text{ h}^{-1}$. Temperature: 613 K. Hydrogen pressure: 50×10^5 Pa. Gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$.

The lowest reactivity among the individual S-compounds is observed for 4,6-dimethyl-DBT, in line with the results of other researchers [15,25,29–31,45]. The reactivity of the substituted individual DBTs appears increasing with the number of substituents. The highest reactivity is estimated for 2,4,6,8-tetramethyl-DBT, next appears the reactivity of 2,4,6-trimethyl-DBT followed by the reactivity of 4-ethyl-6-methyl-DBT which is calculated a little higher than that of 4,6-dimethyl-DBT. The slight superior activity of 4-ethyl-6-methyl-DBT over 4,6-dimethyl-DBT is in agreement with the results of other works [29,30]). The much lower reactivity of 4,6-diisopropyl-DBT and 4,6-diisobutyl-DBT referred by Macaud et al. [49] is attributed to the strong steric effects induced by the structure of the iso-substituents at 4 and 6 positions of DBT.

4,6-dimethyl-DBT appears to be the most refractory compound in this work in agreement with the majority of the published works [4,5,15,30,31,33]. This is also obvious in Fig. 6 where the concentration of each individual S-compound ($C_{i,OUT}$) in heavy gasoil and hydrotreated products is presented in relation with the total sulfur content of the samples ($C_{TOT,OUT}$). As it is shown, for total organic sulfur below 500 ppm, 4-methyl-DBT disappears while the 4,6-alkyl-DBTs seem to disappear in the order 2,4,6,8-tetramethyl-DBT > 2,4,6-trimethyl-DBT > 4-ethyl-6-methyl-DBT > 4,6-dimethyl-DBT [36]. Below 50 ppm total organic sulfur, the 4,6-dimethyl-DBT molecule appears to be the dominant S-compound

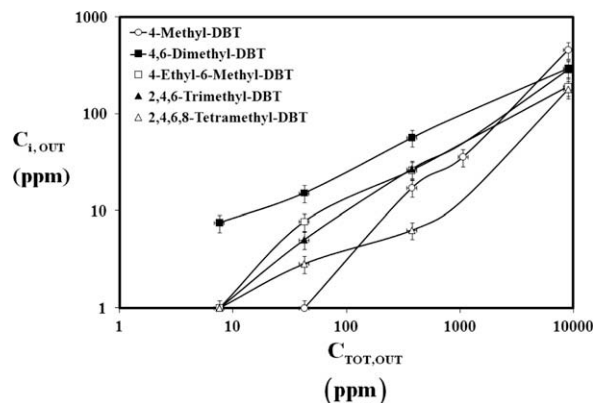


Fig. 6. Concentration of individual sulfur compounds in hydrotreated samples vs. total sulfur content. Hydrotreatment conditions: LHSV: 0.7, 1.0, 2.0, 3.0 h^{-1} . Temperature: 613 K. Hydrogen pressure: 50×10^5 Pa. Gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$.

while in the range of 15–20 ppm_s 4,6-dimethyl-DBT is the only S-compound remaining in the product, in agreement with the published results so far [5,15,19,25,31,33,36]. Taking into account these results and the international requirements for a maximum content of 10 ppm_s in diesel after 2009 [1–4], it is obvious that the understanding of the 4,6-dimethyl-DBT hydrodesulfurization is on the top of the global interest and the successful clarification of its behavior at reaction conditions will help to effectively operate the existing hydrotreaters and achieve even stricter regulations in the future.

A comparison of results obtained in the current work with published results in literature is presented in Fig. 7. In this figure, the normalized apparent first-order reaction rate constants of the various groups and the individual S-compounds are compared with those presented in other works and obtained with different feeds, like gasoil (GO), light cycle oil (LCO), and vacuum gasoil (VGO), when hydrotreated at similar reaction conditions [25,29,30,32]. It must be noticed that in some cases the published data were not referred to the poly-methyl groups as described in this work but to individual S-compounds corresponding to them. In these cases the weighted mean value of the individual compounds corresponding to the group S-compound of the current work has been calculated for the sake of comparison.

From Fig. 7 it is obvious that although the results presented have been obtained with different feeds (LGO, LCO, and VGO), the relative differences in the reactivity of the several DBTs are similar. The most important difference is observed for the relative reactivity of the methyl substituted S-compound group calculated from the results of Ma et al. [32] which appear similar to the mean reactivity of DBT. In the literature there exist results suggesting that the reactivity of alkyl-DBTs with substituents at different to 4 and 6 positions (e.g. 3,7-dimethyl-DBT) may be ever higher than that of DBT [11,17]. This observation is not supported by the results of the current work obtained at 613 K. However, the reactivities of DBT and methyl-DBT group appear to be similar for reaction temperature 563 K, as will be shown later (Figs. 13 and 14).

The results presented in literature mainly concern HDS of DBT, 4-methyl-DBT and 4,6-dimethyl-DBT which are considered as ref-

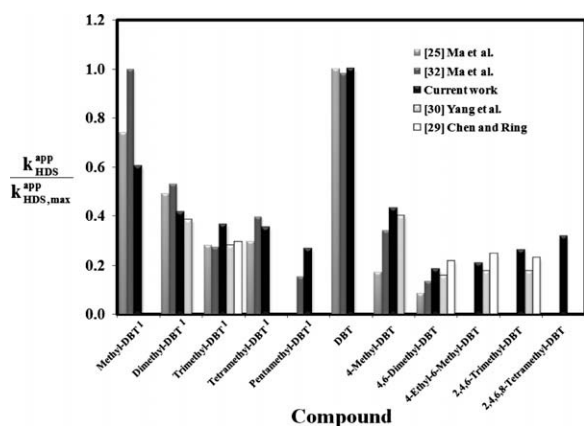


Fig. 7. Normalized apparent reaction rate constants of group¹ and individual DBTs obtained in the current work in comparison with those obtained by other investigators. Experimental conditions of this work: temperature: 613 K, hydrogen pressure: 50×10^5 Pa, gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$. Other works: Ma et al. [25], HDS of VGO at temperature: 633 K and pressure: 69×10^5 Pa; Ma et al. [32], HDS of diesel at temperature: 633 K and pressure: 29×10^5 Pa; Yang et al. [30], HDS of LCO at temperature: 623 K and pressure: 70×10^5 Pa; Chen and Ring [29], HDS of LC-finner LGO treated at: temperature: 648 K and pressure: 69×10^5 Pa. ¹For some group compounds the mean value of reaction rate constant was estimated with the results for individual compounds presented by the publishers. For example Ma et al. [32] presented the reactivities for several dimethyl-DBTs except of 4,6-dimethyl-DBT, thus the mean value of dimethyl-DBT group reactivity was estimated.

erences compounds [4,31]. The reaction rate constants for these compounds obtained in the current work are 0.0045, 0.0019, and 0.0008 g/g_{cat.}/s while the ratios between them are 5.6:2.4:1.0. Kabe et al. [31] have presented similar results (8:3:1) at 623 K for hydrotreatment of a light gasoil with a CoMo/Al₂O₃ catalyst and they claimed that the reaction rate constants of these DBTs are significantly lower than those estimated for pure model compounds hydrodesulfurization [5,50]. This observation clearly indicates that a very strong inhibiting matrix effect on the HDS reaction rates of sulfur compounds exists during reaction from the various molecules present on the catalyst surface [26].

3.2. Hydrogen sulfide effect on the HDS of DBTs

The effect of hydrogen sulfide on the hydrodesulfurization of the various sulfur compounds present in the gasoil was studied at LHSV: 1 h^{-1} , temperature: 613 K, total hydrogen pressure: 50×10^5 Pa and gas to liquid ratio: $600 \text{ Nm}^3/\text{m}^3$. The hydrogen sulfide partial pressure at reactor outlet ($P_{\text{H}_2\text{S,OUT}}$) was controlled by adding dimethyl-disulfide in the liquid feed [11–13]. Because the majority of the S-compounds (about 80%), mainly the less refractory ones, react within the first 20% of the reactor length at the reaction conditions of these experiments, as shown in Fig. 8, it is considered that the partial pressure of hydrogen sulfide at the reactor outlet represents the H₂S partial pressure in the whole catalyst bed. The evolution of H₂S partial pressure along the reactor length shown in Fig. 8 has been predicted by simulating the reactor performance and taking into account the first-order reaction rates for all S-compounds. As shown in this figure, in the first 10% of the reactor length H₂S partial pressure has reached 60% of its maximum value at the reactor exit (point a) while 80% of the maximum H₂S partial pressure is reached at a distance from the inlet corresponding to 20% of the total reactor length (point b).

In Table 2 the effect of hydrogen sulfide on the HDS first-order apparent rate constant is presented. The values given are the ratios of the apparent reaction rate constants of each compound at each hydrogen sulfide partial pressure and the corresponding constants determined at 5.31×10^5 Pa (reference experiment) hydrogen sulfide partial pressure. The experiment performed at 5.31×10^5 Pa hydrogen sulfide partial pressure was considered as the reference experiment because all the S-compounds, except of DBT, are present in the product. From these results it is concluded that the transformation rates of DBTs decrease with the increase of H₂S partial pressure for all the compounds. It is also observed that the effect of H₂S is stronger for the methyl-DBTs and it appears decreasing with the number of substituents. This observation is in agreement with the results of other works studying similar com-

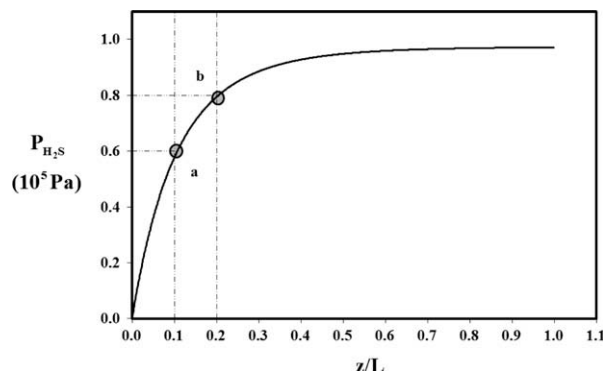


Fig. 8. Partial pressure of hydrogen sulfide vs. normalized reactor length, for desulfurization of a typical gasoil at typical conditions. LHSV: 1.0 h^{-1} . Temperature: 613 K. Total pressure: 51×10^5 Pa. Gas-to-liquid ratio: $600 \text{ Nm}^3/\text{m}^3$. Inlet sulfur concentration: 13,000 ppm.

Table 2
Relative hydrogen sulfide effect on the apparent HDS reaction rate constant of DBTs. Obtained for LHSV: 1.0 h⁻¹, temperature: 613 K, hydrogen pressure: 50 × 10⁵ Pa and gas to liquid ratio: 600 Nm³/m³.

	$P_{\text{H}_2\text{S}}^1 = 0.97 \times 10^5 \text{ Pa}$	$P_{\text{H}_2\text{S}}^2 = 1.82 \times 10^5 \text{ Pa}$	$P_{\text{H}_2\text{S}}^3 = 3.95 \times 10^5 \text{ Pa}$
	$\frac{k_{\text{HDS}}^{\text{app}}}{k_{\text{HDS}}^{\text{ref}}}$ ^a	$\frac{k_{\text{HDS}}^{\text{app}}}{k_{\text{HDS}}^{\text{ref}}}$ ^a	$\frac{k_{\text{HDS}}^{\text{app}}}{k_{\text{HDS}}^{\text{ref}}}$ ^a
Methyl-DBT		1.411	1.033
Dimethyl-DBT	1.315	1.223	1.035
Trimethyl-DBT	1.469	1.111	0.978
Tetramethyl-DBT		1.206	0.935
Pentamethyl-DBT		1.187	1.027
DBT ^b			
4-Methyl-DBT		1.543	1.118
4,6-Dimethyl-DBT	1.525	1.356	1.068
4-Ethyl-6-methyl-DBT	1.324	1.260	1.048
2,4,6-Trimethyl-DBT	1.204	1.197	1.020
2,4,6,8-Tetramethyl-DBT		1.117	0.992

^a The experiment for hydrogen sulfide partial pressure 5.31 × 10⁵ Pa was considered as the reference experiment because all the S-components, except DBT, were present in the products.

^b DBT was not detected in the products obtained at LHSV: 1.0 h⁻¹, temperature: 613 K, hydrogen pressure: 50 × 10⁵ Pa and gas to liquid ratio: 600 Nm³/m³.

pounds in real feeds as well as in feeds composed with model compounds [11–13,31].

Kabe et al. [31] presented results of a light gasoil hydrodesulfurization over a NiMo catalyst. They showed that the retarding effect of H₂S on HDS decreased in the order DBT > 4-methyl-DBT while on 4,6-dimethyl-DBT no effect was detected. They claimed that H₂S inhibits the formation of biphenyls (BPs) through the hydrogenolysis route rather than the formation of tetrahydrodibenzothiophenes and hexahydrodibenzothiophenes (HNS) through the hydrogenation route. Thus they explained that the strong influence of H₂S on the DBT transformation occurred because the direct HDS route prevailed over hydrogenation but for the transition of 4-methyl-DBT and 4,6-dimethyl-DBT the hydrogenation route dominated. Similar conclusions were presented by Meille et al. [11] and Rabarihoela-Rakotovo et al. [13]. On the contrary Chen and Ring [29] claimed that H₂S strongly inhibited DBTs with substituents in 4 and 6 positions than the others and they suggested that H₂S might have stronger inhibited the hydrogenation route than the hydrogenolysis route for a light gasoil hydro-treated with a NiMo catalyst. Similar observations reported by Vradman et al. [27], Lecreany et al. [45], and Kasahara et al. [46].

In any case the differences of inhibition effect of H₂S on the two reaction routes does not explain why the H₂S inhibition decreases with the number of substituents on DBTs either through the direct route or indirect route. The results of Meille et al. [11], Bataille et al. [12], and Rabarihoela-Rakotovo et al. [13] indicate that the inhibition effect of H₂S on the transition of 4,6-dimethyl-DBT through either the direct or indirect route is less than that on DBT. This trend is supported by the results of the current work where the inhibition effect of H₂S on the HDS rate decreases in the order 4,6-dimethyl-DBT > 2,4,6-trimethyl-DBT > 2,4,6,8-tetramethyl-DBT. All these compounds are DBTs with substituents at 4 and 6 positions and the ratio of molecules that react through the indirect route to those reacting through the direct route has to be similar according to the mechanisms presented so far. Thus a more detailed approach is required to answer the question why the effect of H₂S decreases with the increase of the number of substituents.

An answer to the above question could be the competitive adsorption of H₂S and the various DBTs [19,35]. The DBTs may be characterized by different adsorption equilibrium and the more substituted DBTs may be strongly adsorbed on the catalyst sites. Kabe et al. [22] presented results for DBT, 4-methyl-DBT and for 4,6-dimethyl-DBT and they proposed that the adsorption equilibrium decreases in the order DBT > 4-methyl-DBT > 4,6-dimethyl-DBT. In contrast, Ma et al. [51] supported that the adsorbed

amount of DBT was observed to be bigger than that of 4-methyl-DBT and 4,6-dimethyl-DBT. Finally Meille et al. [11] presented results for competitive experiments of model compounds (DBT, 4-methyl-DBT and 4,6-dimethyl-DBT) over a NiMo catalyst and they proposed that all DBTs they studied have similar adsorption equilibrium constants. They claimed that the difference in reactivity must be due to different reaction rates in the transformation of the adsorbed molecule. Similar results are presented by Bataille et al. [12]. Thus the question remains.

For gaining a further insight on the effect of H₂S on HDS rates of the substituted DBTs during hydrotreatment a simplistic kinetic model was employed in this study. A detailed kinetic model describing the transition of DBTs in an oil fraction would require an overwhelming number of rate and adsorption parameters [42] and it could not be so easily used for oil fraction as it is for model compounds feeds. Thus, a simpler technical model was adopted which is based on the pseudo-first order apparent reaction rate constant for each sulfur compound:

$$k_{\text{HDS}}^{\text{app}} = -\ln\left(\frac{C_{i,\text{OUT}}}{C_{i,\text{FEED}}}\right) \cdot \text{LHSV}, \quad (1)$$

taking into account that the apparent reaction rate constant for each sulfur compound can be correlated with the outlet H₂S partial pressure according to the following equation:

$$k_{\text{HDS}}^{\text{app}} = \frac{k_{\text{HDS}}}{1 + a_{\text{H}_2\text{S}}^{\text{app}} \cdot P_{\text{H}_2\text{S},\text{OUT}}}, \quad (2)$$

or,

$$\frac{1}{k_{\text{HDS}}^{\text{app}}} = \frac{a_{\text{H}_2\text{S}}^{\text{app}}}{k_{\text{HDS}}} P_{\text{H}_2\text{S},\text{OUT}} + \frac{1}{k_{\text{HDS}}}. \quad (3)$$

It should be clarified that $a_{\text{H}_2\text{S}}^{\text{app}}$ does not represent the adsorption equilibrium constant of hydrogen sulfide, which is constant and independent of the S-compounds, but it only reflects the effect of hydrogen sulfide on the transformation rate of each S-compound. The term k_{HDS} expresses the independent of H₂S effect reaction rate constant for each DBT transition. Because all the experiments of this section were performed at the same conditions (temperature, hydrogen pressure, gas to liquid ratio) except of the H₂S partial pressure, it is considered that the influence of the possible inhibitors (nitrogen, aromatics) are similar for all the experiments and the H₂S independent term is constant for each sulfur compound.

In Figs. 9 and 10, the reciprocal apparent reaction rate constant (1/ $k_{\text{HDS}}^{\text{app}}$) for the group S-compounds and for the individual S-compounds is plotted against the outlet hydrogen sulfide pressure

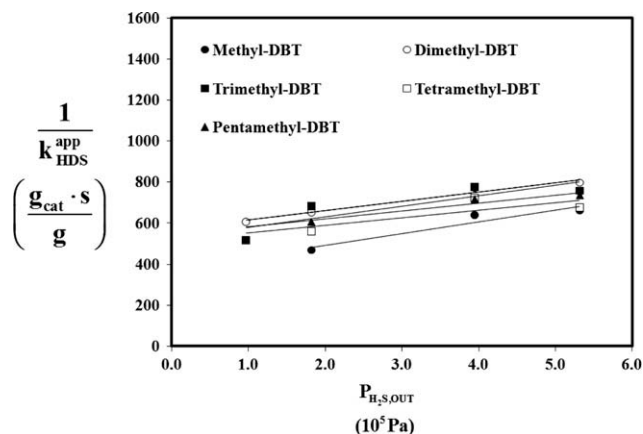


Fig. 9. Reversed apparent reactor rate constant of methyl-DBT, dimethyl-DBT, trimethyl-DBT, tetramethyl-DBT and pentamethyl-DBT groups vs. outlet partial pressure of hydrogen sulfide. LHSV: 1 h^{-1} . Temperature: 613 K. Hydrogen pressure: 50×10^5 Pa. Gas to liquid ratio: $600 \text{ Nm}^3/\text{m}^3$.

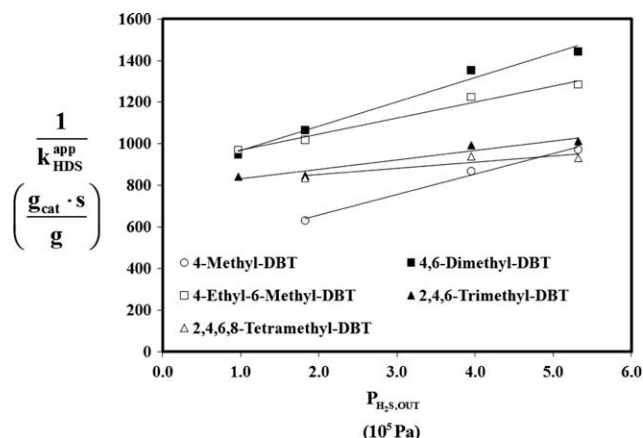


Fig. 10. Reversed apparent reactor rate constant of DBT, 4-methyl-DBT, 4,6-dimethyl-DBT, 4-ethyl-6-methyl-DBT, 2,4,6-trimethyl-DBT and 2,4,6,8-tetramethyl-DBT vs. outlet partial pressure of hydrogen sulfide. LHSV: 1 h^{-1} . Temperature: 613 K. Hydrogen pressure: 50×10^5 Pa. Gas to liquid ratio: $600 \text{ Nm}^3/\text{m}^3$.

($P_{H_2S,OUT}$). A similar approach has been presented by Kabe et al. [22] for individual components showing the linear relation between the reversed apparent reaction rate constant of each S-compound and the hydrogen sulfide pressure. As observed in Figs. 9 and 10, the linearity holds for our results and Eq. (3) relates well the dependence of the HDS rate constants with the hydrogen sulfide partial pressure.

According to Eq. (3) the slopes of the lines ($1/k_{HDS}^{app}$) vs. (P_{H_2S}) express the ratio $a_{H_2S}^{app}/k_{HDS}$ while the intercept expresses the term $1/k_{HDS}$. From the slopes and the state values of the lines in Figs. 9 and 10 the apparent hydrogen sulfide inhibition factor and the independent of H_2S effect reaction rate constant evaluated for each S-compound are calculated. The results are presented in Figs. 11 and 12. These parameters were not possible to be evaluated for DBT because its content in the products of these experiments was negligible.

From the results presented in Fig. 11 it appears that the methyl-DBT group is the most inhibited by H_2S than any other S-compound group. The DBT groups with two and more substituents are affected by H_2S less and the influence of H_2S on their HDS seems to decrease with the number of the component's substituents. An exception to this trend is the dimethyl-DBT group probably due to experimental inaccuracies. The picture is clear in the

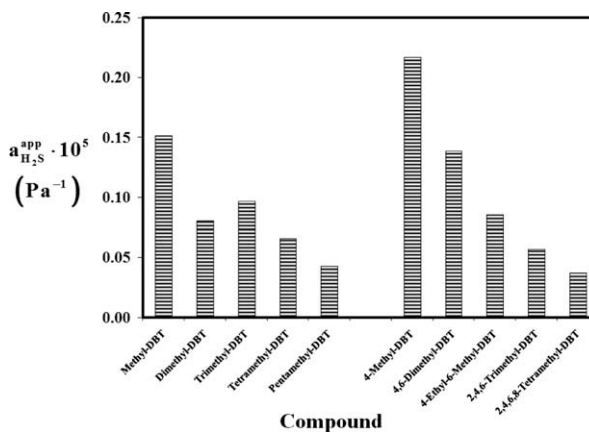


Fig. 11. Apparent hydrogen sulfide inhibition factor ($a_{H_2S}^{app}$) for the S-compound groups and the specific S-compounds. LHSV: 1 h^{-1} . Temperature: 613 K. Hydrogen pressure: 50×10^5 Pa, Gas to liquid ratio: $600 \text{ Nm}^3/\text{m}^3$.

case of the specific compounds. As it is shown in the same figure the highest value of $a_{H_2S}^{app}$ was estimated for 4-methyl-DBT and it decreases with the number of substituents of DBTs. It is also observed that the inhibition factor of groups appears close to that of the individual S-compounds' with the same number of substituents.

In Fig. 12, the independent of H_2S inhibition HDS rate constant of DBTs is presented. As it is shown all DBT groups with more than one substituent are characterized by similar reactivities. Only the methyl-DBT seems to react with higher rates. The reactivity of the various 4,6-alkyl-DBTs seems to be similar but significantly lower than those of group DBTs. The reactivity of 4-methyl-DBT was estimated to be higher than that of the other 4,6-alkyl-DBTs, as indicated in literature. It is also higher than the reactivity of the other S-compound groups indicating that the presence of more substituents affects the reactivity of DBTs independent of their positions. It is obvious that the presence of substituents at 4 and 6 positions affects the reaction rates more significantly than in other positions. This is attributed to steric hindrances, in the basic attack, that are brought about by the alkyl group near the sulfur atom [11,12,21].

Moreover because the value of k_{HDS} for all 4,6-alkyl-DBTs is similar, it is concluded that the rate of transition through the indirect route is the same as the rate of transition through the direct route for all these DBTs.

The observed dependence of the H_2S inhibition effect on the number of substituents in the S-molecule cannot be explained by the contribution of the different reaction routes of direct and indirect HDS. Because the DBTs' adsorption equilibrium constants have been reported to be almost the same [11,12], another approach of the dependence of catalyst activity on the adsorbed and surrounding the active sites hydrogen sulfide to explain the hydrogen sulfide effect on the transition evolution of DBTs is possible. This approach is based on the hypothesis that the activity of the catalyst sites, on which the DBTs molecules are adsorbed, is significantly affected by the H_2S molecules adsorbed on the surrounding catalyst sites. The presence of H_2S in the reacting mixture results in its strong adsorption on the active catalyst sites. The adsorption of H_2S on a site has an impact on the energetic status and consequently on the activity, not only of the site it is adsorbed on but also on the neighboring sites, the impact being reduced with the distance. Therefore, an active site on which a sulfur compound is adsorbed would be influenced by the surrounding active sites having adsorbed H_2S molecules. The smaller the size of the adsorbed sulfur bearing organic compound, the shorter the possible distance of the active site it is adsorbed on from the surrounding sites with

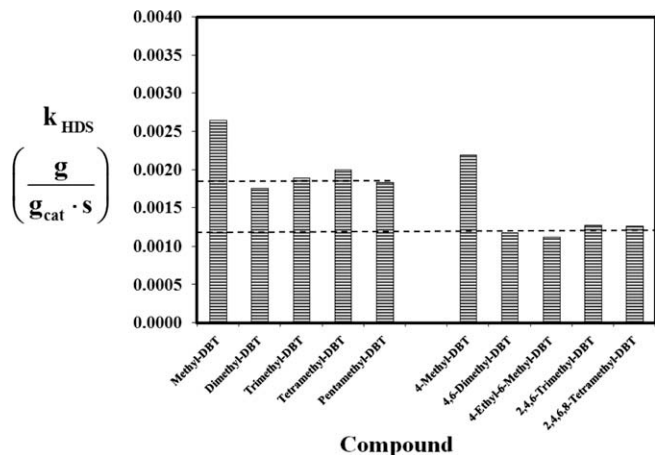


Fig. 12. Independent of H_2S reaction rate constants of DBTs groups and DBTs individual compounds. LHSV: 1 h^{-1} . Temperature: 613 K. Hydrogen pressure: $50 \times 10^5 \text{ Pa}$. Gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$.

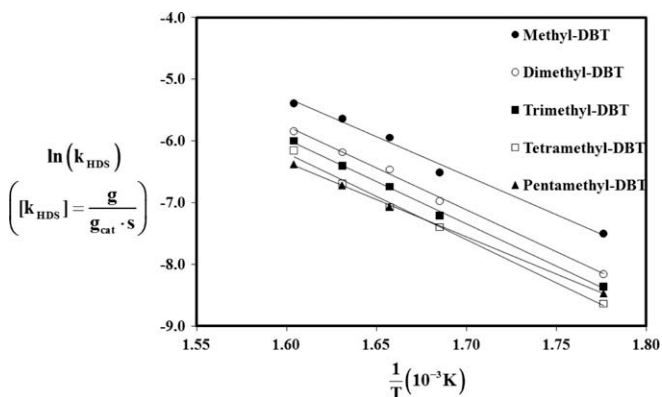


Fig. 13. Arrhenius plots of HDS rate constants of DBTs group S-compounds. Obtained for LHSV: 1.0 h^{-1} (temperature: 563 and 593 K) and 3.0 h^{-1} (temperature: 603, 613 and 623 K), hydrogen pressure: $50 \times 10^5 \text{ Pa}$ and gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$.

adsorbed H_2S on them due to stereo-hindrances and the stronger the impact effect. The higher the H_2S partial pressure in the gas phase the higher the adsorbed H_2S molecules on the active sites surrounding the one having adsorbed the S-bearing organic molecule and thus the stronger the impact of H_2S on the activity of this site. Therefore, as the dynamic diameter of a flat adsorbed DBT molecule increases by increasing the number of substituents, the mean distance of the adsorbed H_2S molecules from the active site on which the S-compound is adsorbed increases and their effect on it decreases. As a result of this the activity of the site with the adsorbed DBTs molecule increases. In Fig. 11 it is obvious that 4-methyl-DBT with the smaller dynamic diameters is more affected by the presence of H_2S than the other DBTs with bigger diameter. In Fig. 11 it is obvious that 4-methyl-DBT with the smaller size is more affected by the presence of H_2S than the other DBTs with bigger size. It is also observed that as the number of substituents on DBTs increases the value of $a_{\text{H}_2\text{S}}^{\text{app}}$ decreases, in accordance with the consideration of the H_2S effect on the HDS rates.

Finally, it must be noticed that the hypothesis referred above can contribute to the explanation of the differences in the relative reactivities of DBT, 4-methyl-DBT, and 4,6-dimethyl-DBT in real feeds and in individual S-compounds feeds presented in the literature [31,50]. In the case of hydrotreatment of real feeds which contain a lot of easily reacting S-compounds (thiophenes, benzothiophenes) [35] the hydrogen sulfide partial pressure

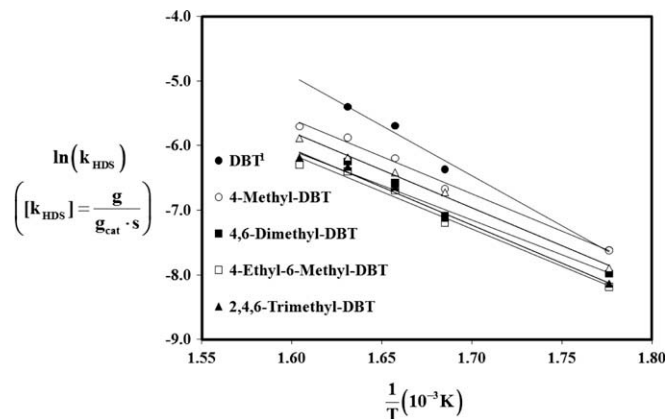


Fig. 14. Arrhenius plots of HDS apparent rate constant of DBT and of 4-methyl-DBT, 4,6-dimethyl-DBT, 4-ethyl-6-methyl-DBT, 2,4,6-trimethyl-DBT, and 2,4,6,8-tetramethyl-DBT. LHSV: 1.0 h^{-1} (temperature: 563 and 593 K) and 3.0 h^{-1} (temperature: 603, 613 and 623 K), hydrogen pressure: $50 \times 10^5 \text{ Pa}$ and gas to liquid ratio: $400 \text{ Nm}^3/\text{m}^3$. ¹The apparent HDS rate constants was used for the estimation of the DBT activation energy because the apparent hydrogen sulfide inhibition factor was not estimated for DBT.

reaches the highest value almost from the first 10–20% sector of the reactor (see Fig. 8), because they are converted at the first part of the reactor very fast. Thus the reaction of DBTs occurs in the presence of high values H_2S partial pressure and the relative activity of more reactive DBT and 4-methyl-DBT than the 4,6-dimethyl-DBT decreases due to the high H_2S partial pressure. In contrast, in the case of hydrotreatment of feeds with individual DBTs the presence of hydrogen sulfide is much less and thus the reactivity mainly of DBT and less of 4-methyl-DBT seems to be much higher than that of 4,6-dimethyl-DBT.

3.3. Apparent activation energy

The apparent activation energies of the group and the individual S-compounds ($E_{\text{HDS}}^{\text{app}}$ (kJ/mol)) was estimated from the HDS experiments performed at five temperatures: 563, 593, 603, 613, and 623 K; two liquid hourly space velocities: 1.0 and 3.0 h^{-1} ; at total hydrogen pressure $50 \times 10^5 \text{ Pa}$ and gas-to-liquid ratio $400 \text{ Nm}^3/\text{m}^3$. The H_2S independent reaction rate constant (k_{HDS}) was calculated for each experiment and each compound according to Eqs. (1) and (2) using the estimated values of $a_{\text{H}_2\text{S}}^{\text{app}}$ obtained before. Moreover, the calculated apparent activation energies of S-compounds are almost the same as those obtained by using the apparent reaction rate constant ($k_{\text{HDS}}^{\text{app}}$), because for the majority of the experimental reaction conditions, hydrogen sulfide partial pressure was almost the same and it was fully developed close to the entrance of the reactor (Fig. 8). For the estimation of the activation energy of DBT the apparent HDS rate constant was used because $a_{\text{H}_2\text{S}}^{\text{app}}$ for this compound was not possible to be estimated.

In Figs. 13 and 14 the Arrhenius plots of the HDS reaction rate constants for the sulfur groups and the individual S-compounds are shown.

The values of the activation energy of the S-compounds calculated from the slopes of the curves in Figs. 13 and 14 are summarized in Table 3. The highest activation energy was calculated for the DBT (129 kJ/mol) while the lowest one was calculated for the 4,6-dimethyl-DBT (89 kJ/mol). The estimated activation energies for the S-compounds groups are in the range of 100–115 kJ/mol while for the individual S-compounds they appear a little lower, in the range of 89–97 kJ/mol. As there is a wide range of activation energy values for DBTs hydrodesulfurization in the literature, our

Table 3

Apparent activation energy values of various DBTs groups and individual S-compound. Obtained for LHSV: 1.0 h⁻¹ (temperature: 563 and 593 K) and 3.0 h⁻¹ (temperature: 603, 613 and 623 K), hydrogen pressure: 50 × 10⁵ Pa and gas to liquid ratio: 400 Nm³/m³.

	$E_{\text{HDS}}^{\text{app}}$ (kJ/mol)
Methyl-DBT	105
Dimethyl-DBT	113
Trimethyl-DBT	114
Tetramethyl-DBT	117
Pentamethyl-DBT	100
DBT ^a	129
4-Methyl-DBT	96
4,6-Dimethyl-DBT	89
4-Ethyl-6-methyl-DBT	96
2,4,6-Trimethyl-DBT	98
2,4,6,8-Tetramethyl-DBT	98

^a The apparent HDS rate constants used for DBT activation energy estimation because apparent hydrogen sulfide inhibition factor did not estimated for it.

values are in agreement with some of them [30,36], mainly the ones having used NiMo catalyst [30,36].

In general, the activation energy of DBTs for the reaction through the indirect route appears to be lower than that through the direct route. Kim et al. [36] show that the activation energy of 4,6-dimethyl-DBT for the reaction through the indirect route is 47,000 J/mol while for the reaction through the direct one is 73 kJ/mol when treatment with NiMo catalyst was attempted. DBT mainly reacts through direct route thus its activation energy is expected to be in the same order and up to 110 kJ/mol.

The results obtained in the current work are in agreement with the analysis above. The highest apparent activation energy was estimated for DBT as it reacts mainly through the direct route. The activation energy for the S-compounds groups appears lower because they consist of several DBTs with substituents at 4 and 6 positions, which mainly react through indirect route, but also of DBTs without substituents at these positions which mainly react through the direct route. Finally the DBTs with substituents at 4 and 6 positions follow mainly the indirect route thus their apparent reaction rate was calculated to be lower than the one presented in literature for similar S-compounds reacting over CoMo catalyst.

4. Conclusion

The deep desulfurization process of heavy gasoil has been studied. The evolution of the removal of five groups with sulfur compounds according to the number of their substituents and six refractory individual sulfur compounds, DBT, 4-methyl-DBT, 4,6-dimethyl-DBT, 4-ethyl-6-methyl-DBT, 2,4,6-trimethyl-DBT, and 2,4,6,8-tetramethyl-DBT was investigated.

The non-substituted DBT appears to be the most reactive molecule among the DBTs of the feed while the methyl-DBT S-compound group appears as the second one in reactivity order. The reactivities of the other S-compound groups seem not to vary significantly. Among the individual compounds, the 4-methyl-DBT appears to be the one with the highest reactivity while the 4,6-dimethyl-DBT appears to be the one with the lowest reactivity over the other compounds. 4,6-dimethyl-DBT, was the dominant compound in the hydrotreated gasoil products which contained total organic sulfur less than 50 ppm. The reactivity of the other substituted DBT specific compounds seem to increase with the number of their substituents. The ratio of the calculated reactivities of the most commonly studied S-compounds DBT, 4-methyl-DBT and 4,6-dimethyl-DBT are 5.6:2.4:1.0, less than those obtained with individual S-compound feeds, in agreement with the literature.

The transformation rate of DBTs decreases with the partial pressure of hydrogen sulfide for all the compounds. However it was found that the DBTs are affected by hydrogen sulfide less when the number of their substituents increases. This was obvious for the groups of sulfur compounds as well as the individual S-compounds although it was more profound for the individual S-compounds. The inhibition effect of individual DBTs seems to decrease in the order 4-methyl-DBT > 4,6-dimethyl-DBT > 2,4,6-trimethyl-DBT > 2,4,6,8-tetramethyl-DBT. The highest inhibition effects were estimated for 4-methyl-DBT and for methyl-DBT group while the group and individual S-compounds with higher number of substituents were characterized by similar inhibition factors in relation to their number of substituents. The independent of H₂S effect reaction rate constants for DBT groups with more than one substituents are similar as well as for 4,6-alkyl-DBTs. The highest values of k_{HDS} were estimated for methyl-DBT and 4-methyl-DBT indicating that the presence of more substituents inhibits the reactivity of DBTs independently of their positions. The reactivities of 4,6-alkyl-DBTs seem to be similar and significantly lower than those of DBT groups probably due to steric hindrance, in the basic attack, generated by the alkyl group near the sulfur atom.

The differences in the apparent reactivities of 4,6-alkyl-DBTs seem to come from the differences on the hydrogen sulfide inhibition. The inhibition effect of hydrogen sulfide on the HDS rates can be explained by the effective size of the adsorbed on the active sites S-molecule that controls the minimum distance of the adsorbed H₂S surrounding the molecule and the active site. The lesser the substituents on the flat mode adsorbed molecule the smaller its size and thus the smaller the mean distance between the adsorbed H₂S molecules and the active site resulting in higher inhibition. It was considered that as the number of substituents on flat mode adsorbed DBTs increases the mean distance of the adsorbed H₂S molecules from the active site on which the S-compound is adsorbed increases and their effect on it decreases. Thus the activity of the site with the adsorbed DBTs molecule increases.

Finally, the highest apparent activation energy calculated for the DBT verifies that DBT reacts mainly through the direct route. The lowest apparent activation energy was calculated for the DBT groups with substituents at 4 and 6 positions showing that they mainly react through the indirect route. Intermediate apparent activation energy values appear for the S-compounds groups because they consist of several DBTs with substituents at 4 and 6 position as well as with DBTs without substituents at these positions. An analysis of activation energies of DBTs for synthetic or real feeds can contribute to defining the reaction scheme of DBTs hydrodesulfurization.

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